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EFFECTIVE SHIELDING VALUES OF THE PHENYL GROUP IN SOME GROUP IVb AND Vb COMPOUNDS

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FOREWORD

This report was prepared as a coordinated study by the Analytical Branch, Materials Physics Division and the Polymer Branch, Non-Metallic Materials Division. The work was initiated under Project No. 7360, "Material Analysis and Evaluation Techniques," Task No. 736005, "Compositional, Atomic and Molecular Analysis," also Project No. 7340, "Non-Metallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers," The work was administered under the direction of AF Materials Laboratory, Deputy for Research and Engineering, Research and Technology Division with Miss Mary T. Ryan and Dr. W. L. Lehn acting as project engineers.

This report summarizes work conducted from October 1962 to June 1963.

ABSTRACT

The effective shielding values of the phenyl group in silanes, germanes, stannanes, amines, phosphines and arsines are calculated from the proton magnetic resonance frequencies of protons attached to the group IVb or Vb element. The effective shielding of the phenyl group appears to be dependent on the electronegativity of the element to which it is bonded. The application of an additivity rule in calculating the frequency of protons in substituted silanes is shown.

This technical documentary report has been reviewed and is approved.

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INTRODUCTION

As methane is successively substituted, a paramagnetic shielding of the remaining protons is generally observed. Meyer and Gutowsky (ref 1), Bothner-By and Naar-Colin (ref 2) and Shoolery (ref 3), as well as others, have studied the proton magnetic resonance spectra of substituted methanes.

Shoolery (ref 3) has proposed an additivity rule for calculating the chemical shift of the protons in substituted methanes. This relationship is

$$\tau = 9.767 - \sum_i \sigma_{i_{eff}}$$

where τ is the chemical shift of the protons in the substituted methane, 9.767 is the chemical shift of the protons in methane and σ_{eff} is the effective shielding constant of the i_{th} group. The chemical shifts are measured in p.p.m. from $(CH_3)_4Si$ which has a τ value of 10.000.

Assuming that electron withdrawal from the carbon atom causes the change in chemical shift, it becomes progressively harder to withdraw electrons as the number of electronegative groups is increased, so that the effective shielding constant for a group is obtained by taking an average of the shifts caused by successive substitutions of the group on methane. The value chosen for the effective shielding constant lies between the values for the first and second substitutions weighed a little more heavily in favor of the first. As pointed out by Jackman (ref 4), the use of Shoolery's additivity rule has been found to reproduce the τ values of some twenty methylene protons with an average deviation of ±0.05 p.p.m.

We have measured the proton magnetic resonance spectra of some phenyl substituted compounds of group IVb and Vb elements and calculated the value of the effective shielding constant of the phenyl group using a method similar to Shoolery's. The values of σ_{eff} for the phenyl group in these compounds appear to be dependent on the electronegativity of the element to which the phenyl group is bonded.

We have estimated the effective shielding constant of the methyl group in some group IVb compounds from chemical shift measurements in the literature and show that the additivity rule applies also to substituted silanes.

EXPERIMENTAL

The proton magnetic resonance spectra of the phenyl derivatives were measured using a Varian A-60 Nuclear Magnetic Resonance Spectrometer. Dilute solutions in CCl_4 or $CDCl_3$ (2-10%) were used and $Si(CH_3)_4$ was added as an internal standard. Several concentrations of each compound were measured and when the chemical shift appeared to vary with concentration, the value extrapolated to zero concentration was used. Since diphenylstannane is unstable in CCl_4 and $CDCl_3$, it was necessary to use benzene as a solvent for this compound.

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MATERIALS

Diphenylsilane, triphenylsilane and diphenylamine were obtained from commercial sources and used without further purification. Aniline and diphenylphosphine were obtained commercially and purified by distillation. Triphenylgermane and diphenylgermane were prepared according to the procedure of Johnson and Harris (ref 5). Diphenylstannane was prepared using the method of Kuivila, Sawyer and Armour (ref 6). Triphenylstannane, prepared according to Tamborski, Ford and Soloski (ref 7) was kindly supplied by these authors. We also wish to thank Dr. D. Seyferth of Massachusetts Institute of Technology for supplying a sample of diphenylarsine.

LITERATURE VALUES

The chemical shifts of the hydride molecules are taken from the literature. The values for silane, ammonia and phosphine are the values for the "non-associated" gaseous state taken from Schneider, Bernstein and Pople (ref 8). These authors measured the chemical shift of simple hydride molecules in the liquid and gaseous states relative to methane gas and their values of the chemical shift for the gaseous state have been converted to τ values.

The value for arsine is taken from Gutowsky and Hoffman (ref 9) who measured the screening constant of liquid arsine as well as several other liquids and gases. Using the relationship of Schneider, Bernstein and Pople (ref 8) that "liquid association shift" = $\delta_{liq} - \delta_{gas} - \frac{2\pi}{3} X_v \times 10^6$, where δ = chemical shift and X_v is the volume susceptibility of the compound, and assuming that the "liquid association shift" of arsine is the same magnitude as that of phosphine, the chemical shift of gaseous arsine was calculated. The volume susceptibility of arsine was calculated from Pascal's constants and from the density relationship for liquid arsine given by Rees and Stewart (ref 10).

The value for stannane is taken from the work of Flitcroft and Kaesz (ref 11).

DISCUSSION

Group IVb Compound

In calculating an effective shielding constant for a group in substituted methanes, the chemical shift of the remaining protons after each successive substitution is measured. Figure 1 shows the effect of the progressive substitution of halogens and of the phenyl group on the chemical shift of the protons in substituted methanes.

The relative position of the curves for the three halogens are in the expected order. The least electronegative halogen, iodine, causes the smallest change in chemical shift. The position of the curve for the phenyl group does not agree with the Taft σ^* values (ref 12) of relative electron withdrawing power of various groups which place the phenyl group at a much lower value than any of the halogens. However, Dailey and Shoolery (ref 13) have measured the electron withdrawal power of substituent groups using an empirical relationship which depends on the chemical shift difference of methyl and methylene protons in substituted ethanes. They place the electronegativity of the phenyl group between bromine and iodine which is the order shown in figure 1 for the substituted methanes.

Assuming that electron withdrawal from the carbon atom in substituted methanes causes the displacement of the proton to lower field, it becomes progressively harder to withdraw electrons as the number of electronegative groups is increased, and the chemical shift difference becomes smaller with increasing substitution. By taking the average of the change in chemical shifts for three substitutions, an effective shielding constant for each substituent can be found. In table 1 are tabulated the changes in chemical shift for each substitution, the average value, and Shoolery's value of the effective shielding constant (σ_{eff}) which is a weighted average.

TABLE 1

Change in Chemical Shift of Methane Protons Upon Substitution

	Cl	Br	I	C_6H_5
$^{\tau}CH_4 - {}^{\tau}CH_3X$	2.79	2.42	1.94	2.10
$^{\tau}CH_3X - {}^{\tau}CH_2X_2$	2.31	2.32	1.71	1.59
$^{\tau}CH_2X_2 - {}^{\tau}CHX_3$	1.97	1.91	1.03	1.54
average	2.36	2.22	1.56	1.74
Shoolery's σ_{eff}	2.53	2.33	1.818	1.832

The τ values of the chemical shift for silane, stannane and the phenyl substituted silanes, germanes and stannanes are shown in table 2.

TABLE 2

τ Values of Protons in Group IVb Hydrides and Phenyl Substituted Group IVb Compounds

	Si	Ge	Sn
$^{\tau}MH_4$	6.77		6.15
$^{\tau}MH_3\Phi$	5.81*		
$^{\tau}MH_2\Phi_2$	5.14	4.86	3.78 (in C_6H_6)
$^{\tau}MH\Phi_3$	4.57	4.27	2.96 (in C_6H_6) 3.17 (in $CDCl_3$)

*Value from Tier's Proton Nuclear Resonance Shielding Values, G. V. D. Tiers Minnesota Mining and Mfg. Co., St. Paul 6, Minnesota.

The changes in chemical shift for each successive substitution for the phenyl substituted Group IVb compounds are shown in table 3.

TABLE 3

Changes in Chemical Shift of Protons in Group IVb Phenyl Substituted Compounds

	C	Si	Ge	Sn
$\tau_{MH_4} - \tau_{MH_3\Phi}$	2.10	.96		
$\tau_{MH_3\Phi} - \tau_{MH_2\Phi_2}$	1.59	.67		
$\tau_{MH_2\Phi_2} - \tau_{MH_3\Phi_3}$	1.54	.57	.59	.92

If Shoolery's method of calculating an effective shielding constant is applied to phenyl substituted silanes, the effective shielding constant of the phenyl group in substituted silanes is approximately .80 compared to a value of 1.83 in substituted methanes. Although a complete series has not been measured for substituted germanes and stannanes the values obtained indicate the shielding constant of the phenyl group is close to the value in substituted silanes.

Webster (ref 14) has studied the proton magnetic resonance spectra of C-H and Si-H protons in a series of methyl, phenyl substituted methanes and silanes and noted that in the carbon series, the change is much larger than in the silicon series. He attributed this to possible $d\pi - p\pi$ bonding between silicon and the phenyl rings. However, his measurements on other trisubstituted silanes indicate that the effective shielding of other groups, as well as the phenyl group, is much lower in silanes than in methanes. For example, if the τ value he gives for $Me_3\underline{SiH}$, 6.149, is put into the equation $\tau = \tau_{SiH_4} - \Sigma\sigma_{eff}$, σ_{eff} for the methyl group is approximately .21 compared with Shoolery's value of .466 for the methyl group in substituted methanes (ref 3).

Flitcroft and Kaesz (ref 11) have measured proton shifts in some methyl stannanes. Their values for $(CH_3)_3\ \underline{SnH}$, $\tau = 5.27$, and $\underline{SnH_4}$, $\tau = 6.15$, put into the equation $\tau = \tau_{SnH_4} - \Sigma\sigma_{eff}$ yields a value of about .29 for the effective shielding of the methyl group.

The effective shielding for both the phenyl group and methyl group in these compounds appears to be in the order of the relative electronegativities of the element to which the group is attached. According to Allred and Rochow (ref 15) these are C > > Sn > Si.

The effect of $d\pi - p\pi$ bonding would be in the same direction as that of the electronegativity effect and it is difficult to evaluate the relative importance of these two effects in determining the shielding constant of the phenyl group. The general reduction in shielding for all groups as shown by the measurements of Webster (ref 14) indicates the importance of the electronegativity effect. However, our measurements indicate that the shielding constant of the phenyl group in germanium compounds is less than that for tin compounds although the electronegativity of germanium is greater than that of tin according to Allred

and Rochow (ref 15). A possible explanation for this would be a decrease in $d\pi$ - $p\pi$ bonding in going from germanium to tin. In a comparative study of π bonding from oxygen to the group IVb elements, West, Baney and Powell (ref 16) have reported a decrease in going from silicon to germanium to tin.

Group Vb Compounds

Our measurements of some phenyl substituted group Vb compounds indicate an effect similar to that found for the group IVb compounds. Table 4 lists the τ values of the protons in the compounds studied.

TABLE 4

τ Values of Some Group Vb Hydrides and Phenyl Substituted Group Vb Compounds

	N	P	As
$^{\tau}M\underline{H}_3$	9.82	8.29	7.17
$^{\tau}M\underline{H}_2\Phi$	6.42		
$^{\tau}M\underline{H}\Phi_2$	4.37	4.74*	5.02

*Center of Doublet, P-H Coupling Constant 219 cps.

Since the complete series is not available, these may be compared by considering the change in chemical shift upon substitution of two phenyl groups. These values are shown in table 5.

TABLE 5

Change in Chemical Shift of Protons in Group Vb Phenyl Substituted Compounds

	N	P	As
$^{\tau}M\underline{H}_3$ - $^{\tau}M\underline{H}\Phi_2$	5.45	3.55	2.15

The effective shielding of the phenyl group would be approximately one-half the values shown in table 5.

Additivity of substituent groups in group Vb compounds would not be expected on the basis of limited data available in the literature on the chemical shifts of protons attached to nitrogen in primary and secondary amines. Pople, Bernstein and Schneider (ref 17) have summarized the measurements on alkyl and aryl amines. They show the proton in secondary amines at a higher field than the protons in primary amines in contrast to the measurements reported here. However, the measurements in the literature have in many cases been made on pure liquids or concentrated solutions so that the effect of hydrogen bonding on the chemical shift values needs clarification. Our measurements which were extrapolated to zero concentration indicate a successive decrease in the shielding of the protons attached to nitrogen as the number of phenyl substituents is increased.

Although further work on substituted amines and phosphines is needed to confirm this, on the basis of our present measurements, it appears that the shielding of the phenyl group in Vb compounds, as shown in table 5, is also in the order of the electronegativities of the elements to which the phenyl group is attached. According to Allred and Hensley (ref 18), the order of electronegativities is N > > P > As.

SUMMARY

The effective shielding of the phenyl group is lower in silanes, germanes and stannanes than in methanes. It is also lower in phosphines and arsines than in amines. On the basis of limited data available in the literature, it appears that other groups also exhibit a lower effective shielding in silanes and stannanes than in methanes. The dependence on electronegativity which the effective shielding values show indicate the shielding values may be a measure of the ability of the element to transmit the inductive effect of an electronegative substituent.

The effective shielding constants of substituent groups in silanes, as in methanes, can be used to determine the τ values of the remaining protons. For example, using the values of σ_{eff} of .80 for the phenyl group and .21 for the methyl group and the relation that $\tau = \tau_{SiH_4} - \sum_i \sigma_{i\,eff}$ the calculated values for the proton attached to silicon in $Me_2Ph\,SiH$ and $MePh_2SiH$ are 5.55 and 4.96, respectively. The observed values, as reported by Webster (ref 14), for these compounds are 5.57 and 5.08.

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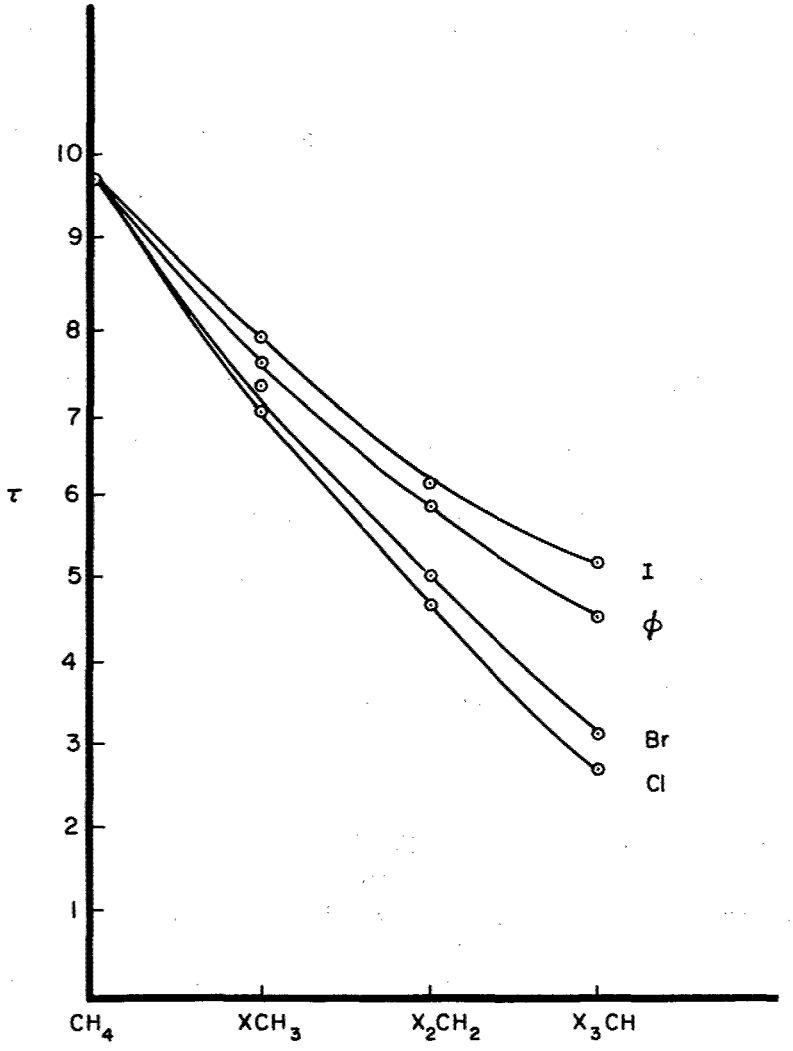

Figure 1. τ Values of Protons in Substituted Methanes (a similar curve for the halogens referenced to cyclohexane appears in ref 17, p. 279.)